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REPORT NO. 37

PARTIAL OXIDATION
OF PROPANE

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BY

C. N. Satterfield
R. E. Wilson

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Division of Industrial Cooperation   Cambridge, Mass

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Partial Oxidation of Propane

by

C. N. Satterfield and Robert E. Wilson[1]

Department of Chemical Engineering

Massachusetts Institute of Technology

Cambridge, Massachusetts

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Abstract

The oxidation of propane was studied extensively in a
flow system at inlet temperatures of 475°C, the temperature
region considered most suitable for hydrogen peroxide formation
and for which only limited information was previously available.
Studies were conducted also at 375°C, thus bracketing the
temperature region in which the reaction has a negative temperature
coefficient. The major objective was to clarify the reaction
mechanism, with particular reference to the role of hydrogen
peroxide. The results indicate that under the conditions of this
work a key reaction is that of the propyl free radical with
oxygen which may follow two alternate paths, one forming oxygenated
organic products, and the other forming propylene and the
perhydroxy free radical. This radical in turn reacts with
propane, or another hydrocarbon, to form hydrogen peroxide and
a free radical. The negative temperature coefficient of the
reaction rate can be explained on the basis of the two alternate

reactions of the propyl radical with oxygen. With an increase
in temperature, the reaction which forms propylene was found to
increase, relative to that forming oxygenated organics.
However, the propylene and perhydroxyl radical formed by the
first reaction are known to be less active in continuing chain
reactions than the oxygenated organic species alternately
formed, thus causing a decrease in the overall rate of reaction.

The above conclusions are of considerable significance in
extending the knowledge of the reaction mechanism of hydrocarbon
oxidations. The results are also of interest in evaluating the
industrial potential of these reactions as methods for manufacture
of chemicals.

The oxidation of propane with pure oxygen was studied in a flow reactor under conditions such that appreciable yields of hydrogen peroxide and other intermediate products could be isolated. The objectives of this work were to clarify the reaction mechanism, with particular reference to the role of hydrogen peroxide, and to obtain information which would aid in an evaluation of the industrial potential of the reaction. The experimental conditions covered inlet gas temperatures of 350 to 475°C., propane-oxygen mole ratios of 5.6 to 12.3, and reaction times of 3.2 to 11.8 seconds.
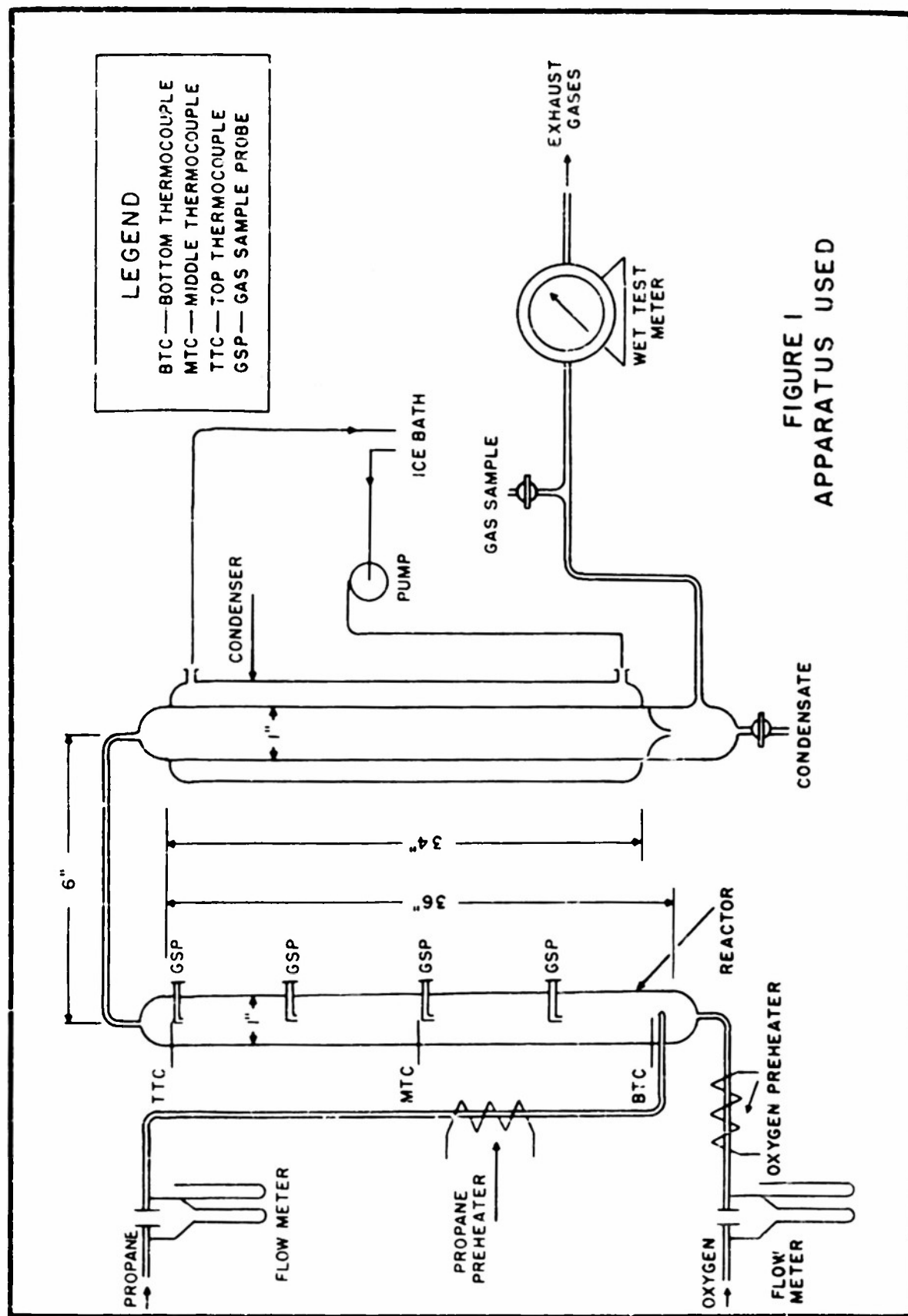
Propane is of particular interest in a study of hydrocarbon oxidation mechanisms, since it is the lowest molecular weight hydrocarbon containing both primary and secondary carbon atoms, and thereby typifies the homologous series of straight chain saturated hydrocarbons. Propane is also readily available from petroleum operations and thus would be a suitable raw material for a possible partial-oxidation process for the production of hydrogen peroxide.

A majority of the previous work reported in the literature on propane oxidation was conducted at temperatures substantially below 400°C and was concerned primarily with the mechanism of the reaction (2), (10), (19), (21), (22), (23). Although considerable speculation existed concerning the exact nature of the reaction, it is now generally believed that at these relatively low temperatures one of the important steps involves

the formation of an alkyl hydroperoxide or an alkyl peroxy
radical, which in turn decomposes leading to the formation
of aldehydes, methyl alcohol, carbon monoxide, and certain
free radicals (17). Propylene, ethylene, hydrogen, methane,
and hydrogen peroxide have also been found among the intermediate
products under these conditions.

The previous work at temperatures exceeding 400°C. was
concerned mainly with the industrial potential of the reaction
for production of hydrogen peroxide, and suggested that as
the temperature increased the yields of olefins and water increased
at the expense of the oxygenated organic products (3), (8),
(13), (15). It also appeared that hydrogen peroxide yields were
increased at the higher temperature, but the limited information
obtained did not permit an interpretation of the reaction
mechanism. One of the important objectives of the present work
was to obtain a sufficient quantity of accurate, quantitative
data under conditions that would permit elucidation of the
mechanism of this reaction at temperatures exceeding 375°C.

It was observed by Pease (21) and Kooijman (13) that in
a flow system the overall reaction rate has a negative temperature
coefficient in the range of 370° to 430°. In the present work
quantitative information was obtained at temperatures below and
above the range of the negative temperature coefficient, to
permit interpretation of this phenomenon.

LEGEND

BTC—BOTTOM THERMOCOUPLE
MTC—MIDDLE THERMOCOUPLE
TTC—TOP THERMOCOUPLE
GSP—GAS SAMPLE PROBE

FIGURE I
APPARATUS USED

Experimental Procedure

The equipment consisted of a tubular Pyrex flow reactor, preceeded by separate electrically-heated preheaters for each gas and followed by a tubular surface condenser cooled with water at approximately 0°C. The arrangement of the equipment is shown in Figure 1. The reactor shape was such that the flow characteristics of the gas approximated that of slug flow. Propane of 99% minimum purity and oxygen of 99.5% purity were employed as the reactants. The residence time of the gases within the reactor was varied by changing the inlet gas flow rates. Rapid mixing of the inlet gases was obtained by introducing the propane axially into the oxygen stream through 40 small orifices located on the upper surface of a spiral-shaped glass tube, whose plane was perpendicular to the axis of the reactor.

Temperature control in the reactor itself was obtained by insulating the reactor and winding it with a compensating electrical heater. By adjusting the voltage input, it was possible to maintain essentially isothermal conditions throughout the reactor at low to moderate rates of reaction. At high rates of reaction, such as at 475°C, a substantial temperature increase occurred along the reactor due to the heat of reaction. For this reason, both the inlet and outlet temperatures have been listed in Tables II and III, which give the experimental data and results. During each run the

equipment was allowed to come to a steady state temperature condition before gas and liquid samples were collected. The liquid sample was collected over a measured time interval during which the exhaust gas sample was collected in periodic increments. The exhaust gas flow rate was measured by a wet test meter.

For every run, the gas sample was analyzed volumetrically by chemical absorption for carbon dioxide, propylene, ethylene, oxygen, and carbon monoxide. Hydrogen was determined by passage over heated copper oxide, but it was present in such small quantities that analysis for it was not made in all the runs.

Samples of residual gas from two of the runs (Nos. 65 and 71) were quantitatively analyzed by infra-red absorption*, after removal of oxides of carbon, olef'ns and oxygen. The instrument had been standardized with mixtures containing known quantities of the following components: methane, ethane, propane, n-butane, iso-butane, neo-pentane, iso-pentane, and 2, 3-dimethyl butane. In both cases, the two components methane and propane accounted for over 98 per cent of the total saturated hydrocarbons. Consequently in a number of other

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*   This was kindly performed for us by the Research Laboratories Division of the General Motors Corporation.

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runs quantitative analysis was made for methane at M.I.T. by
use of a Baird Associates infra red spectrophotometer
standardized with mixtures of methane and propane after
similar removal of the same components. In all runs except
numbers 65 and 71, all remaining gas after analysis for
specific components is reported in the column headed "C_3H_8"
in the Tables of Results. In all cases this gas consists
predominantly of propane but it is seen that it may or may
not include small quantities of hydrogen and methane, depending
upon whether or not one or both of these species were analyzed
for individually. The various procedures for the gas analysis are
given by Burke, Starr, and Tuemmler (1).

The condensate from each run was analyzed for total
peroxide, total aldehyde, formaldehyde, and methanol. The
remainder was assumed to be water. In conjunction with the
overall study, various analytical methods for the condensate
were evaluated. This evaluation, and the recommended analytical
procedure which was used here are presented in detail elsewhere
(27). Briefly, the total peroxide was determined iodometrically
using 56% hydriodic acid as the reagent and glacial acetic
acid as the solvent. Formaldehyde was determined colorimetrically
using acidified Shiff's reagent. Acetaldehyde was calculated
as the difference between formaldehyde and the total aldehyde,
the latter being analyzed by the hydroxylamine method. The
methyl alcohol was separated from the condensate by distillation,

after first converting the aldehydes to acid salts with sodium
hydroxide-hydrogen peroxide solution, and then determined
colorimetrically with ceric nitrate reagent.

Results

In order to determine what saturated hydrocarbons are
formed during the reaction, two samples of residual gas were
analyzed in detail by infra red absorption as described above,
after first removing oxides of carbon, olefins, and oxygen
by chemical absorption. The analyses were made on the residual
gas from runs 65 and 71, which were conducted at 475°C inlet
temperature with a mole ratio of propane to oxygen of 8:1. The
results are presented in Table I, together with four tests
made on known samples, which compare/with actual compositions.
reported
The results indicate that methane is the principal saturated
hydrocarbon formed, but that minor amounts of ethane are also
formed along with traces of n-butane and iso-butane and possibly
iso-pentane. The most important result from the standpoint of
the reaction mechanism is that 2, 3-dimethyl butane, which
would be present if propyl radicals combined with each other,
is not formed. The manner in which these saturated hydrocarbons
actually found are postulated to be formed is discussed below.

The experimental data, presented in Table II, include
for each run the inlet and outlet gas temperatures, the flow
rates, and the composition of the exhaust gas from the condenser
and that of the condensate. The figures in the column designated

Table I

Paraffin Gas Analysis by Infrared Absorption

Compound	Known I Actual %	Known I Found %	Known II Actual %	Known II Found %	Known III Actual %	Known III Found %	Known IV Actual %	Known IV Found %	Paraffin of Run 65 %	Paraffin of Run 71 %
Propane	56.0	58.5	72.8	75.0	88.2	88.7	92.2	91.5	87.0%	78.5%
Methane	20.0	19.0	9.5	9.5	9.8	9.5	4.8	3.8	4.2	10.0
Ethane	4.0	3.5	4.2	4.0	0	0.3	0	0.2	0.5	1.1
n-Butane	4.0	3.2	2.5	1.5	0	0	0	0.1	0.3	0.2
iso-Butane	4.0	4.0	2.5	3.0	0	0	0	0	0.5	0.5
neo-Pentane	4.0	2.7	2.5	2.0	0	0	0	0.6	0	0
iso-Pentane	4.0	3.8	3.5	2.8	0	0.3	0	0.3	0.5	0.7
2,3,-Dimethyl butane	4.0	3.7	2.5	2.8	0	0	0	0	0.1	0
Water	0	0	0	0	2.0	1.5	3.0	3.2	3.0 estimated	3.0 estimated
Total	100.0	98.4	100.0	100.6	100.0	100.3	100.0	99.7	96.1	94.0

TABLE II

TABLE OF EXPERIMENTAL DATA

Run No.	TEMPERATURE °C Inlet	Outlet	FLOW RATES Gm Mole/Hr C₃H₆	O₂	Exhaust Gas	Gm/Hr Condensate	EXHAUST GAS Percent (Dry Basis) CO	CO₂	Mole C₃H₆	C₂H₄	H₂	CH₄	COMPOSITION C₃H₆	O₂	CONDENSATE Weight Percent COMPOSITION CH₃OH	HCHO	CH₃CHO	H₂O₂	H₂O
A7	751 ± 2	390 ± 1	6.69	1.15	7.76	0	0	0	0.1	0	--	--	84.7	15.2	--	--	--	--	--
A5	375 ± 2	390 ± 2	6.19	1.10	7.28	7.05	0.25	0.3	1.2	0.15	0.6	--	84.9	12.6	18.8	19.4	17.6	10.9	37.5
A4	400 ± 2	402 ± 2	5.94	1.05	7.18	7.63	0.35	0.2	0.75	0.1	--	--	84.7	14.0	3.7	18.8	19.4	20.8	82.1
A6	426 ± 1	422 ± 1	5.76	1.03	6.85	0	0	.1	0.9	0	--	--	84.8	14.2	--	--	--	--	--
A4	450 ± 2	452 ± 1	5.52	0.97	6.60	3.10	0.1	0	1.75	0.25	--	--	84.5	13.6	1.6	4.0	14.5	20.6	59.5
7a	473 ± 1	500 ± 13	5.33	0.98	6.80	28.1	8.2	0.3	18.0	10.0	--	0.2	71.0	0.8	7.2	7.1	1.8	1.2	82.7
A8	375 ± 2	390 ± 7	6.19	1.10	7.28	7.08	0.25	0.3	1.2	0.15	0.6	--	84.9	12.6	18.8	19.8	17.8	10.9	37.5
A0	376 ± 1	419 ± 2	5.65	1.01	6.51	11.0	1.0	0.25	2.5	0.2	0.5	--	84.2	11.8	18.8	19.1	12.8	10.6	43.5
A1	375 ± 1	419 ± 3	5.08	0.90	5.79	10.0	0.9	0.27	2.6	0.25	0.7	--	84.6	10.8	18.8	17.0	14.7	11.8	61.7
A8	375 ± 1	415 ± 2	4.38	0.78	5.02	9.8	1.0	0.25	2.8	0.87	--	--	85.1	10.4	13.7	16.5	15.8	13.1	61.3
A12	375 ± 1	417 ± 1	3.60	0.64	3.99	9.9	1.5	0.1	3.45	0.57	0.3	0.2	84.5	9.6	18.8	15.0	14.7	13.9	42.1
A6	375 ± 3	380 ± 7	3.61	0.66	3.92	14.8	2.6	0.4	4.05	0.63	0.5	--	85.2	6.7	22.4	15.5	14.6	10.8	36.7
A5	375 ± 3	393 ± 10	3.61	0.66	3.83	16.1	3.0	0.5	4.35	0.66	1.0	--	84.2	6.0	22.2	16.0	13.8	11.5	36.9
C7	376 ± 2	379 ± 5	3.11	0.55	3.25	16.1	4.2	0.5	5.4	0.7	2.0	1.1	83.2	3.0	21.0	16.3	9.5	11.7	61.3
C8	375 ± 2	379 ± 9	2.52	0.44	2.60	15.0	5.0	0.6	6.4	1.2	--	1.0	84.9	1.0	21.1	16.0	12.8	12.5	38.0
76a	475 ± 1	485 ± 3	8.04	1.44	9.85	5.0	0.1	0.3	2.5	0.2	--	--	82.8	18.5	1.5	8.0	11.3	20.1	63.1
78b	475 ± 2	500 ± 5	6.96	1.23	8.10	9.6	0.2	0	4.2	0.6	--	--	82.7	12.3	1.2	3.2	10.7	18.3	66.6
75c	475 ± 1	520 ± 16	6.17	1.08	7.77	18.3	0.7	0.3	7.6	2.5	--	--	80.7	8.0	5.8	3.8	9.7	12.8	68.3
A1a	476 ± 1	540 ± 9	6.16	1.08	6.72	26.3	2.5	0	10.1	5.6	0.7	--	77.2	3.8	5.7	5.8	6.0	0.6	76.1
A1b	476 ± 2	566 ± 10	6.16	1.08	7.07	32.9	3.9	0	12.0	9.5	--	4.2	73.5	1.0	5.6	6.7	3.3	2.2	82.2
A00	473 ± 1	478 ± 7	6.16	1.08	7.29	31.9	4.1	0.3	12.7	10.5	0.9	5.7	70.5	0.8	7.0	9.3	0	2.5	81.2
A0a	476 ± 1	403 ± 7	5.92	1.04	7.07	30.6	4.7	0.3	13.7	11.0	1.5	5.7	68.5	0.3	6.3	8.6	0	1.2	80.1
A9b	475 ± 1	600 ± 13	5.33	0.94	6.40	28.1	4.2	0.3	18.0	10.0	--	7.0	71.0	0.4	7.7	7.1	1.8	1.2	82.7
A2a	475 ± 2	466 ± 3	8.02	0.96	8.85	7.06	0.4	0	2.8	0.5	--	--	87.8	8.5	2.1	3.4	10.8	18.7	64.9
A14	477 ± 1	500 ± 3	7.53	0.90	8.30	11.8	0.7	0	4.8	1.0	--	0.65	86.0	6.8	3.1	3.2	10.2	16.2	67.4
52b	474 ± 2	538 ± 7	6.73	0.85	7.45	16.7	1.0	0	6.8	2.7	0.2	--	85.2	4.0	5.1	3.8	9.5	11.9	69.6
A4e	475 ± 2	585 ± 10	6.57	0.79	7.16	23.4	2.2	0.1	9.7	5.6	--	4.2	77.2	0.9	6.8	4.9	4.1	6.2	78.0
A1b	476 ± 1	560 ± 8	6.16	0.78	6.83	22.1	2.5	0.1	10.0	7.1	--	5.7	78.3	0.3	7.2	5.0	4.6	2.3	80.9
A8b	477 ± 1	550 ± 5	5.61	0.67	6.26	19.9	2.7	0.1	10.0	8.0	--	7.0	71.9	0.3	7.8	5.6	2.7	1.7	82.6
76a	475 ± 2	482 ± 5	6.98	0.57	7.66	4.29	0	0	3.0	0.9	--	--	90.5	5.7	1.6	2.3	1.8	17.5	71.8
77a	475 ± 1	484 ± 4	6.81	0.53	7.04	5.12	0.3	0	3.4	0.8	--	--	90.1	5.4	1.7	4.5	6.2	17.6	69.0
75b	475 ± 2	496 ± 8	5.78	0.87	6.25	8.82	0.3	0.2	5.1	1.6	--	--	88.7	4.1	4.6	4.6	8.0	18.1	69.7
77b	475 ± 2	500 ± 3	5.29	0.33	5.66	9.90	0.4	0.2	6.3	2.2	--	--	88.2	2.6	6.8	5.7	7.2	12.9	69.4
75a	475 ± 2	> 500	4.72	0.38	5.17	10.7	0.7	0.2	7.6	3.3	--	--	86.0	1.6	4.5	5.0	5.4	6.8	78.3
76b	475 ± 1	> 500	4.01	0.32	4.57	9.5	0.9	0.3	9.3	7.0	--	7.0	82.0	0.4	7.8	6.8	1.8	3.2	82.1
A5	475	> 500	6.90	0.94	--	--	1.1	0.4	6.4	4.3	--	3.7	83.5	0.6	--	--	--	--	--
71	475	> 500	4.09	0.74	4.61	12.0	2.4	0.3	10.0	7.9	0.4	8.0	69.9	0.3	--	3.9	4.7	3.3	--
72	475 ± 1	> 500	5.78	0.75	6.14	20.8	1.2	0.2	9.7	4.8	--	3.2	79.3	1.6	5.8	4.6	4.3	17.0	64.3
74	475 ± 1	> 500	4.78	0.60	5.47	17.1	2.0	0.6	10.9	6.4	--	5.6	71.7	0.7	6.0	7.1	0.4	1.7	8.3

* (C₃H₆ + H₂)   • (C₃H₆ + CH₄)   • (C₃H₆ + CH₄ + H₂)

FIGURE 2

PRODUCTS OF PROPANE OXIDATION

INLET TEMPERATURE – 475°C
PROPANE : OXYGEN — 5.6:1

⊙ — H_2O
▢ — C_3H_6
▼ — C_2H_4
● — CO
× — O_2

⊙ — H_2O_2
▢ — CH_3CHO
▼ — HCHO
● — CH_3OH

TOTAL PRODUCT COMPOSITION–MOLE %

OXYGEN REACTED – % OF INLET
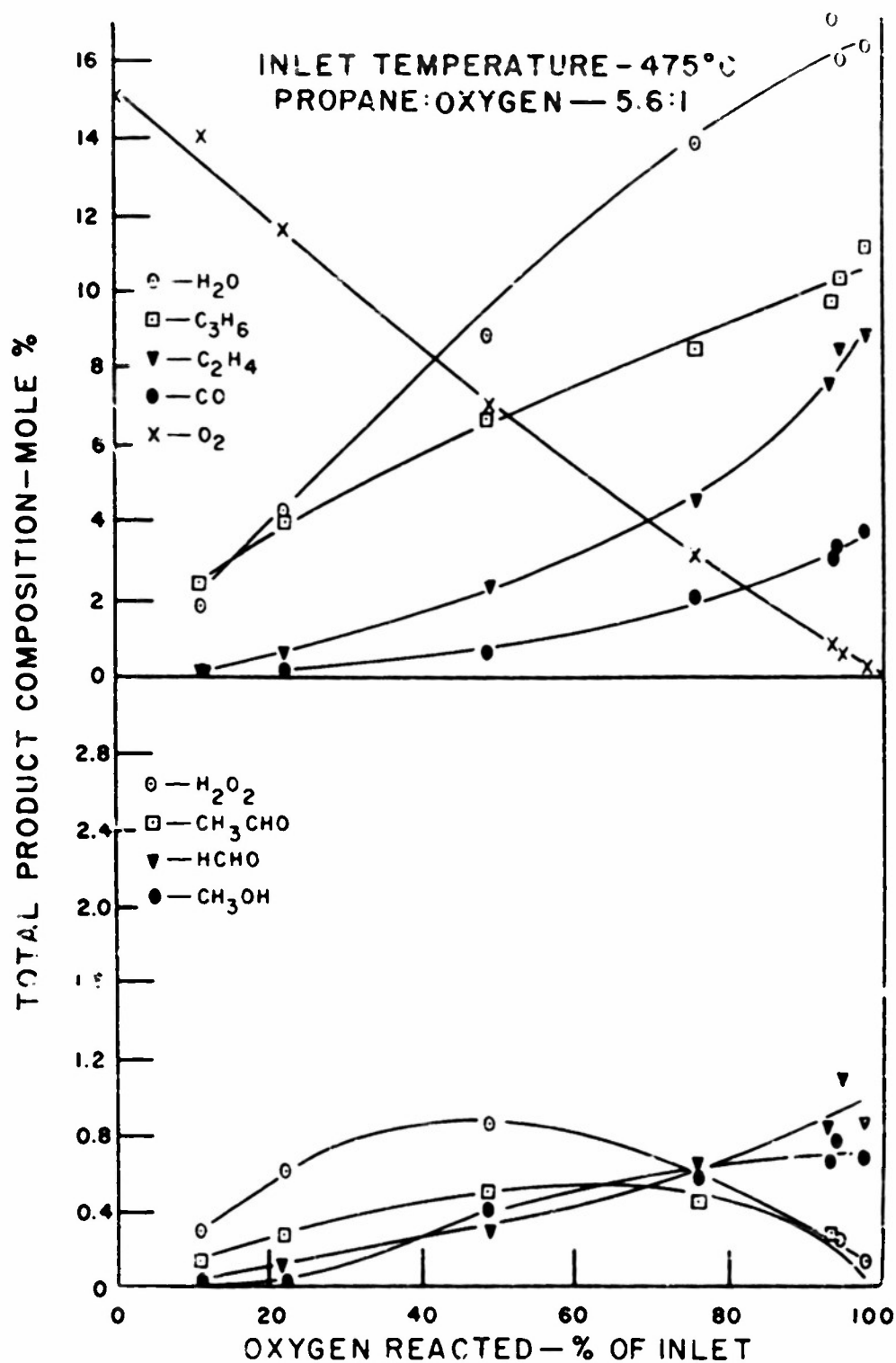
FIGURE 3
PRODUCTS OF PROPANE OXIDATION
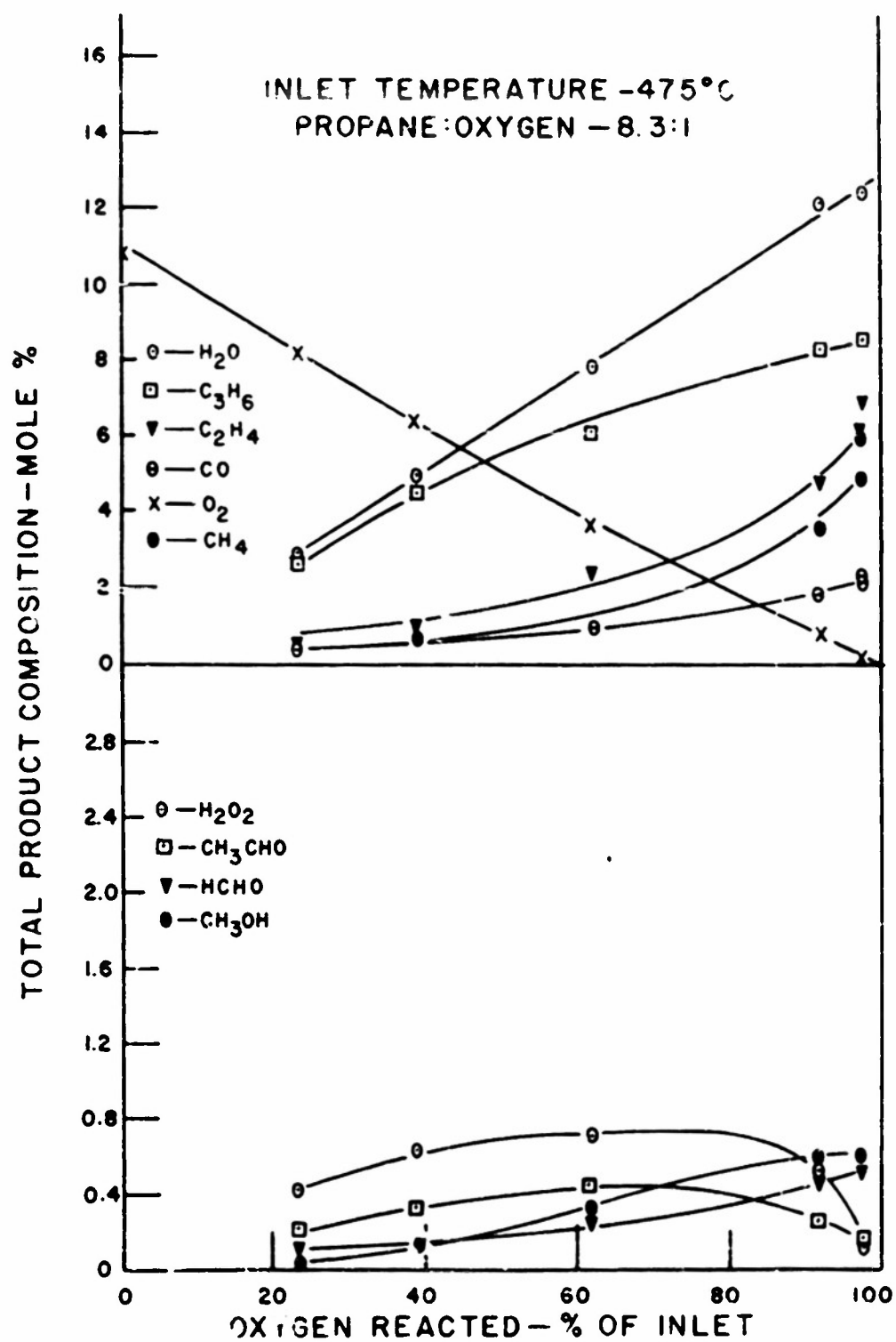
FIGURE 4
PRODUCTS OF PROPANE OXIDATION

INLET TEMPERATURE — 475°C
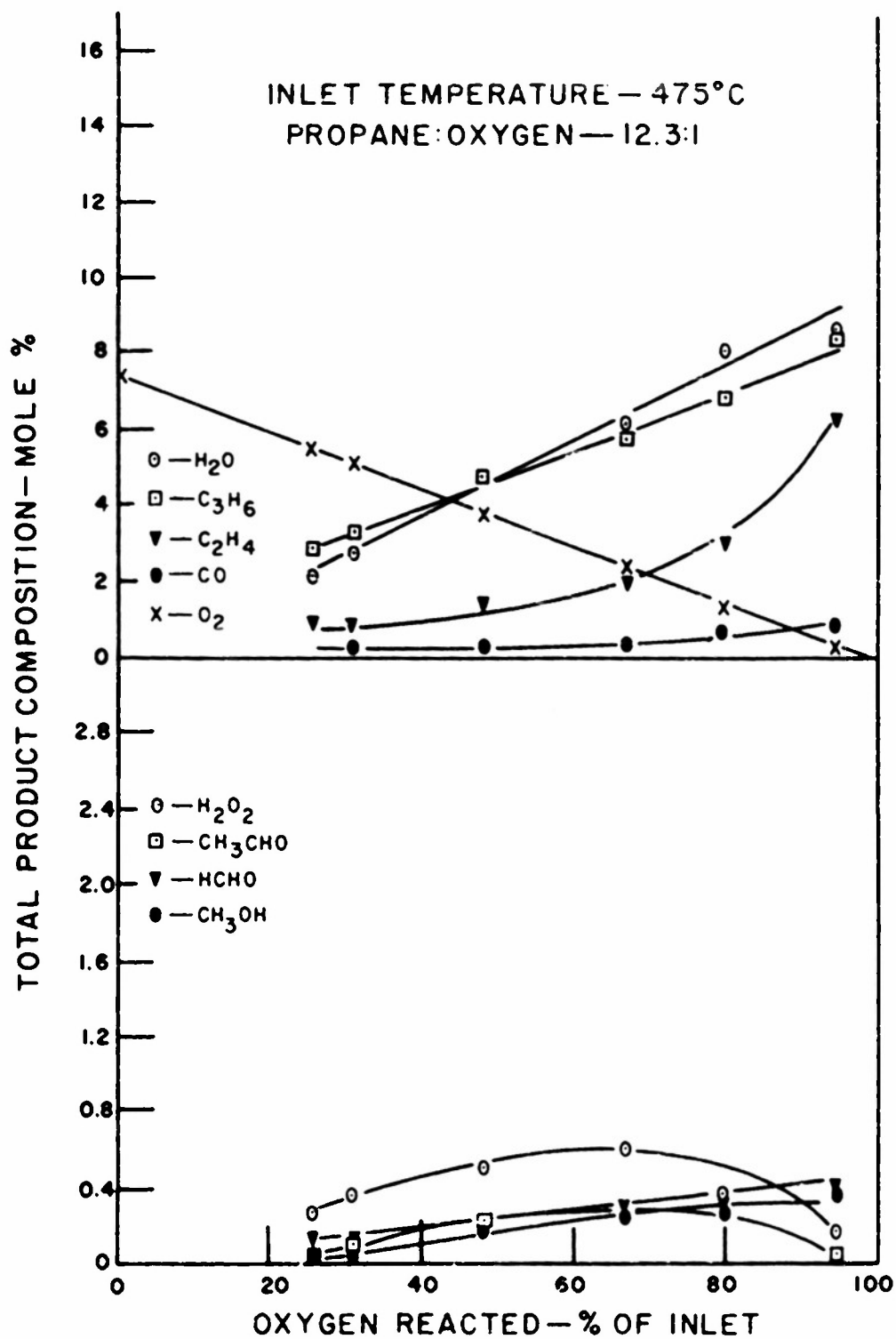PROPANE : OXYGEN — 12.3:1

FIGURE 5
PRODUCTS OF PROPANE OXIDATION

as the "propane concentration" in the exhaust gas were obtained by difference and, as described above, may include not only propane but small amounts of hydrogen, and/or methane as well, depending upon the run.

The data given in Table II were employed in the calculation of the total product composition presented in Table III. These data represent the total gas stream composition before condensation, assuming no reaction occurred in the condenser.

The significance of the results is best seen by plotting the product composition as a function of the percent of the inlet oxygen reacted, for each of four different inlet conditions studied. This has been done in Figures 2 to 5. The concentrations of propane, hydrogen, carbon dioxide, and methane have been ommitted from the figures. The method of plotting used in the figures gives a better correlation of the data than a plot using residence time as the abscissa since, as is characteristic of chain reactions, slight changes in flow rate or temperature may cause a pronounced change in the extent of reaction observed. As a specific example of the time scale involved, at 475°C. and a propane:oxygen mole ratio of 5.6, the apparent induction period was about 3 seconds: at 3.7 seconds, 22% of the inlet oxygen had reacted; at 4.0 seconds, 97% of the oxygen had reacted.

The two products formed in greatest quantities were water and propylene; however, at the higher reaction temperature,

considerably more ethylene, propylene, and water were formed, but less oxygenated products. These results can be observed in Figures 2 and 3 which compare inlet temperatures of 375° and 475°C respectively. It should be noted that as reaction progresses at 475°C the concentrations of hydrogen peroxide and acetaldehyde pass through a maximum value, while all other product concentrations increase continuously. The effects of a change in inlet oxygen concentration at 475°C are shown in Figures 3, 4, and 5. A decrease in oxygen concentration decreased the reaction rate and also caused a proportionate decrease in the concentrations of the oxygenated organic products.

The existance of a negative temperature coefficient for the reaction rate was investigated using a 5.6:1 ratio of propane: oxygen. As the inlet gas temperature was increased from 350°C, the amount of oxygen reacting in 4.8 to 4.9 seconds increased from 2% at 350° to a maximum of 18% at 375°C, declined to a minimum of 5% at 425°, and then increased to 10% at 450° and to 97% at 475°. These results are very similar to those of Kooijman (13), who reported a negative temperature coefficient for a 9:1 mixture in the range of 375° to 430°C.

All of the data presented in this report were obtained with all of the exit gas leaving at the top of the reactor, as i. shown in Figure 1.

Since the reaction time was varied by varying the flow
rates of the inlet gases, this raises the question of whether
the observed results were due in part to changes in the
mixing characteristics of the mixer at the bottom of the
reactor. To answer this question, preliminary studies were
conducted in which a portion of the gas was withdrawn through
one of the gas sample ports. By this means the residence time
could be changed without changing the inlet flow rates. A
comparison of the data for runs at the same residence time but
with linear flow rates differing by nearly 100%, indicated a
slightly increased amount of reaction at the higher flow rates,
which was probably due to the change in heat transfer characteristics.
There were no changes in product composition other than those
caused by differences in the extent of reaction, thus indicating
that the rate of mixing was not a limiting factor on the
reaction as studied here.

Discussion

Some insight into the reaction mechanism involved here
may be obtained by a consideration of first, the quantitative
yields of the various products, second, the effects of oxygen
concentration and reaction temperature upon the yields of the
various products, and third, the heats of reaction and the
energies of activation of the various possible reaction steps
which could account for the results observed. The reaction is

free radical in nature, presumably proceeding through the
propyl free radical. The free radical nature of the reaction
is evidenced by such characteristics as the apparent induction
period. In the discussion below, the important reactions have
been given arabic numbers and are summarized in Table V. Those
reactions considered of minor importance in the over-all mechanism
here are designated by a lower-case letter.

Formation of the Olefins

Chernyak and Shtern (2) propose that the olefins are formed
by the thermal decomposition of the propyl free radical, the
n-propyl forming ethylene and the iso-propyl forming propylene.

$$n - C_3H_7^{\cdot} \longrightarrow C_2H_4 + CH_3^{\cdot} \qquad (1)$$

$$iso - C_3H_7^{\cdot} \longrightarrow C_3H_6 + H^{\cdot} \qquad (a)$$
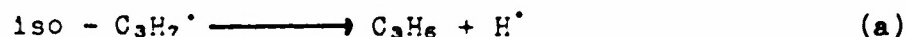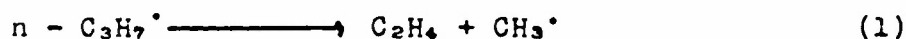
The occurrence of reaction (1) here is evidenced by the appreciable
yield of methane that was obtained in this investigation and is
also demonstrated directly by the work of Paneth and Lautsch
(20) who decomposed tetra-n-propyl lead at about 400°C. They
attempted to identify the products of the decomposition by means
of lead, zinc, and antimony mirrors; the only identifiable organo
metallic compounds were methyl compounds. They therefore
concluded that any propyl radicals formed decomposed rapidly by
means of reaction (1).

The reactions of the iso-propyl radical are not as clearly
defined as those of the n-propyl radical. The topic has been
reviewed by Steacie (29), who concluded that the iso-propyl is
somewhat more stable than the n-propyl radical and that reaction

(a), due to its endothermicy, would not be important. The conclusion that secondary alkyl radicals are more stable than primary is supported by reports concerning the behavior of the butyl free radical (25). Di-n-butyl mercury and di-sec. butyl mercury were decomposed by passing the vapors at about 3 mm. pressure through a Pyrex tube heated to 490°C. Three-quarters of the n-butyl radicals decomposed into ethylene and the ethyl free radical, a reaction equivalent to reaction (1). The sec-butyl radical was more stable and reacted 77% by combination and disproportionation reactions similar to reactions (b) and (c), listed below. The fact that the yield of hydrogen in the present investigation was only a small fraction, approximately one-tenth, of the propylene yields indicates that reaction (a) is of no importance in the present case. There is considerable evidence that the iso-propyl radical enters into combination, disproportionation, and addition reactions (29).

$$2 \; iso - C_3H_7{}^{\cdot} \longrightarrow C_6H_{14} \qquad (b)$$

$$2 \; iso - C_3H_7{}^{\cdot} \longrightarrow C_3H_6 + C_3H_8 \qquad (c)$$

$$iso - C_3H_8 + C_2H_4 \longrightarrow C_5H_{11}{}^{\cdot} \qquad (d)$$
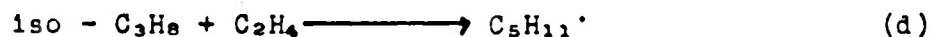
The literature reports indicate, however, that the formation of propylene by reaction (c) is accompanied by the formation of hexane by reaction (b). The fact that in this present work no 2,3 - dimethyl butane was found among the products of oxidation at 475°C indicates that reaction (c) is not the source of the propylene. The infrared analysis also detected,

at most, only traces of pentanes, thus enabling one to neglect
reactions of the type (d). The work of Rice and Evering (24)
suggests that the iso-propyl radical decomposes at 450° to
550°C to form ethylene and methyl radicals, and thus reaction
(1) may not be limited solely to the n-propyl radical.

Since water is the major product of the reaction, it is
logical to seek a connection between its formation and that
of propylene. There is no simple reaction that will directly
relate the two products. It is important to note also that
hydrogen peroxide has been reported as a major product at times
when large quantities of olefins were produced. For example,
Lacomble (15) reported a hydrogen peroxide yield of 0.52 moles
per mole of propane reacted, employing a reaction temperature of
470°C, a propane:oxygen ratio of 9:1 and a residence time of
5 seconds. Cook (3) reported a maximum hydrogen peroxide yield
of 0.30 moles per mole of propane reacted, when using a 5.7:1
ratio of propane:oxygen at 527°C. The first step in the formation
of hydrogen peroxide, a reaction of the propyl radical with
oxygen, was suggested tentatively by Lewis and Von Elbe (17)
for the ethane - oxygen reaction.

$$C_3H_7^{\cdot} + O_2 \longrightarrow C_3H_6 + HO_2^{\cdot} \qquad (2)$$
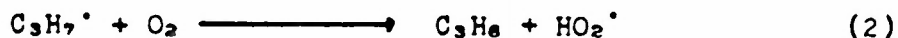
The reaction is approximately thermo-neutral; it is 18 kcal
exothermic if the calculation is based on the $HO_2^{\cdot}$ dissociation
energy reported by Walsh (30) and 6 kcal endothermic if based

on the dissociation energy reported by Evans, Hush, and Uri
(5). The propyl radical and oxygen also react by an alternate
path to form oxygenated organic products.

$$C_3H_7{}^\cdot + O_2 \longrightarrow \text{oxygenated organic} \quad (e)$$
$$\text{products}$$
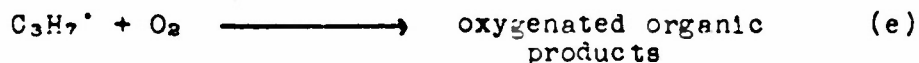
This reaction will be discussed in greater detail below.

The set of reactions, (2) and (e), predicts that the
fraction of the propyl radicals reacting with oxygen which form
propylene should be a function of the temperature only. This
assumes that the relative rates of reactions (2) and (e) are
determined by the individual energies of activation. This
fraction was calculated from the data in the following manner:
first, the number of moles of propyl free radicals reacting
by (2) was assumed equal to the propylene formed; second, the
total number of moles of propyl radicals reacting with oxygen
(the sum of reactions (2) and (e)) was calculated to be the total
moles of propane reacted minus the moles of ethylene formed.
The ethylene is subtracted from the total because it is believed
to be the only product formed from the propyl radical which does
not involve reaction with oxygen. The results of the calculation
are presented in Figure 6 in which the ordinate represents the
moles of propylene formed per mole of propyl radical reacting
with oxygen. It is seen that this fraction is independent of
the inlet oxygen concentration and of the extent of the reaction,
but varies with the temperature. This is exactly as predicted
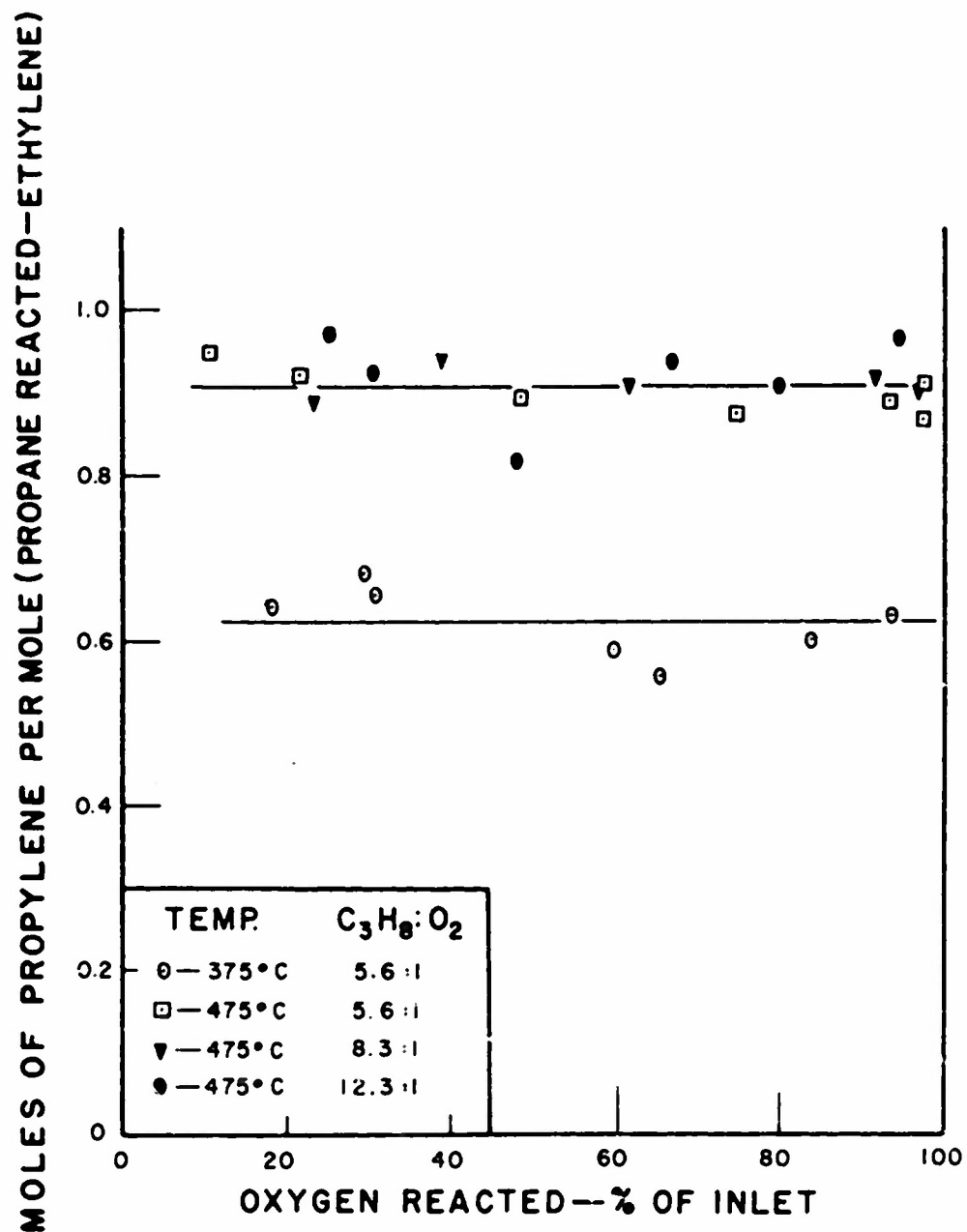
FIGURE 6

TEST OF POSTULATED MECHANISM
REPRESENTED BY EQUATIONS 2 AND e

by the set of reactions, (2) and (e).

The formation of hydrogen peroxide and water

Hydrogen peroxide can be formed from two hydroxyl radicals only by a wall reaction at very low temperatures (26). The logical source for hydrogen peroxide is the perhydroxy free radical formed in reactions (1) and (2). The radical has been considered relatively unreactive (17), and it therefore may be though that the formation of hydrogen peroxide takes place at the wall.

$$2 \; HO_2 \cdot \xrightarrow{\text{wall}} H_2O_2 + O_2 \tag{f}$$
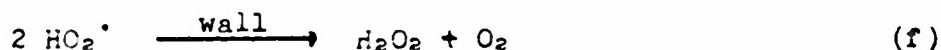
This reaction however must be discarded in favor of a gas phase reaction after a consideration of the experimental results of other workers. For example, Geib and Harteck (7) found that under conditions where atomic hydrogen alone does not react with hydrocarbons, atomic hydrogen plus oxygen will give a rapid reaction, suggesting a reaction of the following type.

$$C_3H_8 + HO_2 \cdot \longrightarrow C_3H_7 \cdot + HO_2 \cdot \tag{3}$$
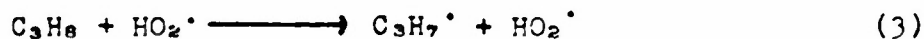
Additional evidence for the gas phase reaction, (3), is given by the work of Lacombie (15), who conducted the oxidation of propane in a spherical shell, introducing the reactants tangentially at the outer circumference and withdrawing the products from the center. Under these conditions of essentially homogeneous gas phase reaction, he recovered a relatively high yield of hydrogen peroxide. Jost (12) concluded that the

perhydroxy radical will react with hydrogen and hydrocarbons
at reasonably low temperatures. In light of the above
discussion the present authors conclude that hydrogen peroxide
is formed during the reaction by means of reaction (3).

If all perhydroxyl disappeared by reaction (3) and if the
hydrogen peroxide were stable and did not react further, its
production would equal that of the propylene. The fact that
the maximum yield actually obtained in this work was 0.25 moles
of hydrogen peroxide per mole of propylene is probably due to
rapid disappearance of hydrogen peroxide after being formed,
as shown by the shape of the curves in Figures 3,4, and 5.
There are two paths by which hydrogen peroxide may dissapear;
first, it may decompose at the wall, or second, it may react
in the gas phase with the other organic compounds present.
There is no direct evidence for or against the latter reaction,
but it should be noted that hydrogen peroxide will react with
aldehydes in the liquid phase (4), (14).   There is, however,
considerable evidence that hydrogen peroxide decomposes
heterogeneously in the gas phase.

$$H_2O_2 \xrightarrow{\quad wall \quad} H_2O + 1/2 \; O_2 \qquad (4)$$
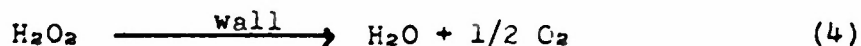
For example, when Harris (9) passed hydrogen peroxide vapors
through a potassium chloride-coated tube, the hydrogen peroxide
was completely destroyed. When using a clean Pyrex tube,
a large fraction of the peroxide passed through undecomposed.
In a reaction tube coated with potassium chloride, Pease and

Munro (23) failed to recover peroxides from propane oxidation, but did recover peroxides when using a clean Pyrex tube. Kooijman (13) reported that washing the reactor tube with hydrofluoric acid increased the yield of hydrogen peroxide from propane oxidation. Cook (3) reported that a coating of boric acid or a borate salt increased the yield. It was observed during the present work that higher yields were obtained when the reactor was new than when it had been in use for some time. The reactor surface undoubtedly plays an important role in the disappearance.of hydrogen peroxide.

Water is also formed by the reaction of the hydroxyl radical with propane, or another hydrocarbon, to form water and a free radical.

$$C_3H_8 + OH^\bullet \longrightarrow C_3H_7^\bullet + H_2O \tag{16}$$
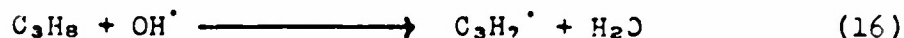
The reaction is exothermic by 32 kcal/mole and has an activation energy estimated by McDonald and Schalla (18) to be 2 to 5 kcal.

Formation of the oxygenated organic products

The exact nature of reaction (e), which forms the oxygenated organic products, will now be discussed in greater detail. Lewis and Von Elbe (17) have reviewed the information available in the literature and propose that the isopropyl radical reacts as follows:

$$iso - C_3H_7^\bullet + O_2 \longrightarrow iso - C_3H_7OO^\bullet \tag{5}$$

$$iso - C_3H_7OO^\bullet \longrightarrow CH_3CHO + CH_3O^\bullet \tag{6}$$
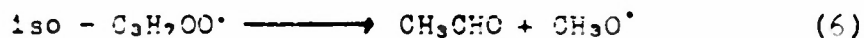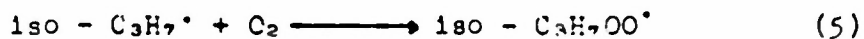
The methoxy radical enters into two competing reactions, one
with oxygen and one with propane.

$$CH_3O^\cdot + C_3H_8 \longrightarrow CH_3OH + C_3H_7^\cdot \tag{7}$$

$$CH_3O^\cdot + O_2 \longrightarrow CO + H_2O + OH^\cdot \tag{8}$$
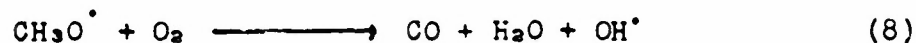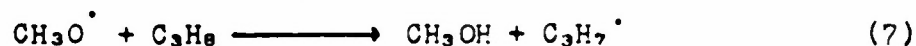
The two reactions (7) and (8) account for the fact that the
methanol yield increases rather sharply as the reaction progresses,
as can be seen in Figures 2 and 3. A similar result was
reported by Pease (22) and Harris and Egerton (10).

The fact that Pease and Munro (22) did not detect propionaldehyde
as a product of propane oxidation is accounted for by the
postulated reactions of the n-propyl radical.

$$n-C_3H_7^\cdot + O_2 \longrightarrow n-C_3H_7OO^\cdot \tag{9}$$

$$n-C_3H_7OO^\cdot \longrightarrow \left[CH_3CH_2CHO\right] + OH^\cdot \tag{10}$$

$$\longrightarrow C_2H_6 + CO \tag{11}$$
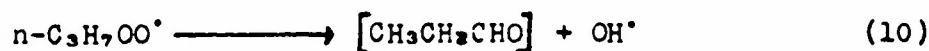
The infrared analysis of the paraffin gas from run no. 71
disclosed that it contained approximately one percent of ethane,
an amount sufficient to account for the extent of reactions
(10) and (11).

The shape of the concentration curves for acetaldehyde
indicates that it enters into further reactions, a conclusion
supported by the work of Chernyak and Shtern (2), who added
acetaldehyde as a diluent and found that its final concentration
was not increased. The decomposition of acetaldehyde at 400°C
is almost entirely a free radical reaction (6).

$$CH_3 CHO + R^\cdot \longrightarrow \left[CH_3 CO^\cdot\right] + RH \tag{12}$$

$$\longrightarrow CH_3^\cdot + CO \tag{13}$$
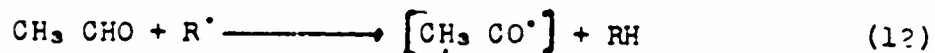
In the presence of oxygen and propane the methyl radical
would participate in two competing reactions.

$$CH_3^\cdot + C_3H_8 \longrightarrow CH_4 + C_3H_7^\cdot \tag{14}$$

$$CH_3^\cdot + O_2 \longrightarrow HCHO + OH^\cdot \tag{15}$$
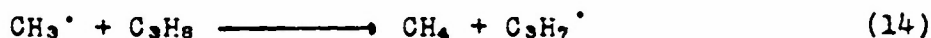
Steacie (29) has reported activation energies of 1.5 kcal for
reaction (15) and 6 to 8 kcal for reaction (14). Due to
the lower activation energy of reaction (15) one would expect
a considerable fraction of the methyl radicals, formed by
both reactions (1) and (13), to be oxidized to formaldehyde,
even in a fuel-rich system.

Pure formaldehyde in the vapor state is more stable than
acetaldehyde, but in the presence of free radicals its
decomposition and oxidation must be considered. The results
of the present work cannot add to the excellent discussion of
Lewis and Von Elbe (17). It is important to note that the small
quantity of hydrogen may have been formed by the decomposition
of the formyl radical.

$$HCO^\cdot \longrightarrow H^\cdot + CO. \tag{18}$$

The calculations of Lewis & Von Elbe indicate that (18) is
endothermic by 25 kcal. The decomposition is quite possible
at temperatures over 400°C in systems having a deficiency of
oxygen.

The theoretical yield of water and hydrogen peroxide

The validity of the postulated mechanism can be further
tested by calculating the yield of water and hydrogen peroxide

which would be expected in terms of the quantities of the
other products which were actually found. In developing
the desired expression the water or peroxide that is formed
by the chain initiating reaction, (1), is neglected, and it
is assumed first, that all hydroxyl radicals react to form
water, second, that all perhydroxy radic.ls react to form hydrogen
peroxide by reaction (3), and third, that the decomposition
of hydrogen peroxide proceeds entirely by reaction (4). Those
reactions which form hydroxyl radicals or water directly are
reaction (10), which forms an equivalent amount of ethane,
reaction (8), which forms one hydroxyl radical and one water
molecule, and reaction (15), which forms an equivalent amount
of formaldehyde. The set of reactions (2), (3), and (4), forms
a quantity of water and hydrogen peroxide equal to the
propylene formed. By summing all of these reactions the
following expression is derived for the total water plus hydrogen
peroxide:

$$N_{H_2O} + N_{H_2O_2} = N_{C_3H_6} + N_{C_2H_6} + 2N_{(reaction(8))} + N_{total \ HCHO}$$

The set of reactions, (6), (7), and (8), specifies that
the number of moles reacting by (8) will be equal to the
total acetaldehyde formed minus the methanol formed.

$$N_{(reaction \ (8))} = N_{CH_3CHO \ found} + N_{CH_3CHO \ reacted} - N_{CH_3OH}$$

A carbon monoxide balance on reactions (8), (11), (13), and (18) results in the following expression:

$$N_{(\text{reaction (8)})}= N_{\text{total CO}}-N_{H_2}-N_{CH_3CHO \text{ reacted}}-N_{C_2H_6}$$

Eliminating the unknown quantity, $N_{CH_3CHO \text{ reacted}}$, results in the following expression for the number of moles reacting by reaction (7):

$$N_{(\text{reaction (8)})}= 1/2\Big[N_{CH_3CHO \text{ found}}+N_{\text{total CO}}-N_{CH_3OH}$$
$$-N_{H_2} -N_{C_2H_6}\Big]$$

Since the formaldehyde has been considered to react only by reactions (17) and (18), the total amount of formaldehyde formed can be expressed as the sum of the formaldehyde found plus the hydrogen found. The total carbon monoxide is represented by the sum of CO and CO_2. Substituting into the original expression for total water and hydrogen peroxide results in the final expression containing only quantities which were determined by analysis of the products.

$$N_{H_2O} +N_{H_2O_2} =N_{C_3H_6} +N_{HCHO} +N_{CH_3CHO} +N_{CO} +N_{CO_2} -N_{CH_3OH}$$

The results of the calculation are presented in Table IV in which the water calculated to be formed from the oxygenated organics alone is also listed for comparison with the total

Table IV

Test of Postulated Mechanism from Observed Yields of Water Plus Hydrogen Peroxide

Run No.	Inlet Temp. °C	% Inlet Oxygen Reacted	Calc'd H₂O* from react-ions (8), (10), (15)	H₂O found* by analy-sis	Total Calc'd H₂O + H₂O₂*	H₂O + H₂O₂ found* by analysis
88	375	18.4	1.1	2.0	2.2	2.3
90	"	29.9	1.8	3.8	4.1	4.3
91	"	31.2	1.9	3.7	4.3	4.2
92	"	34.1	2.0	4.1	4.6	4.8
93	"	42.0	2.3	5.3	5.4	6.2
96	"	60.0	3.0	6.5	6.5	7.5
97	"	65.7	3.5	7.3	7.2	8.5
95	"	83.3	4.3	9.8	8.7	11.3
94	"	94.0	5.2	9.8	10.3	11.5
78a	475	11.1	0.3	1.8	2.7	2.1
78b	"	22.0	0.6	4.2	4.6	4.8
79a	"	48.6	1.3	8.8	8.0	9.7
81a	"	75.5	2.6	13.8	11.0	14.4
81b	"	93.5	3.6	17.1	13.3	17.4
80b	"	94.6	3.8	16.1	14.1	16.4
80a	"	97.8	4.2	16.4	15.3	16.5
79b	"	97.3	3.9	16.4	15.4	16.5
82a	"	23.2	0.6	2.8	3.2	3.2
83a	"	38.8	0.9	5.0	5.4	5.6
82b	"	61.8	1.3	7.8	7.4	8.5
84a	"	91.8	2.1	12.1	10.4	12.6
83b	"	97.5	2.3	12.4	10.8	12.6
84b	"	97.2	2.4	12.5	11.0	12.6

76a	475	25.5	0.1	2.2	3.1	2.5
77a	"	30.9	0.5	2.7	3.8	3.1
75a	"	48.2	0.7	4.8	5.5	5.3
77b	"	67.0	0.9	6.2	6.7	6.8
75a	"	79.7	1.2	8.1	8.0	8.5
76b	"	94.5	1.2	8.5	9.6	8.7
73	"	86.0	1.7	10.0	10.0	11.4
74	"	93.8	2.4	12.6	11.7	12.7

*moles per 100 moles of total product

amount of water which was actually formed. The most significant fact is that the formation and oxidation of the aldehydes accounts for no more than fifty percent of the water actually formed. This is a strong indication that a reaction, such as (2), connecting water and olefin production is very necessary. The calculated values of water plus hydrogen peroxide in Table IV are often slightly higher at the early stages of reaction and slightly lower at the later stages than the values actually found. This trend is easily accounted for by the fact that first, some of the water passes through the condenser as vapor and second, the chain initiating step, (1), has been neglected in the calculation. There is also the possibility that a small fraction of the hydrogen peroxide decomposed in the gas phase by splitting into two hydroxyl radicals, a reaction possessing an activation energy of approximately 45 kcal (16).

The negative temperature coefficient

The negative temperature coefficient of the reaction rate is an important phenomenon which must be explained by the oxidation mechanism. In the region from 375° to 425°C the rate was found to decrease with increasing temperature. Judging from the changes in product composition in Figures 2 and 3, the shift in reaction which occurs with increasing temperature is an increase in reaction (2) and a decrease in reactions (5) and (9). A decrease in the over-all reaction rate

would occur if the products of reaction (2), propylene and
perhydroxy radicals, were less active in continuing the chain
than the products of reactions (5) and (9), which are aldehydes,
methoxy radicals, and hydroxy radicals. Propylene is known
to inhibit free radical reactions (11), while aldehydes
participate readily. The perhydroxy radical is considered to
be less reactive than the hydroxy radical (17). It therefore
appears that the decrease in the over-all rate of reaction
was caused by the increased production of propylene with
increasing temperature.

Industrial aspects of the reaction

Although appreciable yields of useful chemical products
are obtained, it is very difficult at the present time to
evaluate the industrial possibilities of the process. Several
very important questions remain to be answered. The manner in
which the reactor surface influences the reaction is not
fully understood. It is known, however, that the yield of hydrogen
peroxide varies greatly depending on the amount and kind of
surface present and would probably be higher for reactors of
lower surface-volume ratios and constructed with more inert
surfaces. The effects of adding end products to the feed
stream, such as would occur on recycling, have not been fully
investigated. Reports indicate that dilution of the feed stream
with olefins has adverse effects (3,15), indicating the necessity

for considerable treatment of the recycle gas. The separation of the condensate into marketable chemicals presents a difficult problem that requires further clarification. A study of this separation problem is reported elsewhere (28).

The highest yield of hydrogen peroxide obtained here was 0.195 mole per mole of oxygen reacted or 0.12 mole per mole of propane reacted. This occurred at 475°C and with a propane: oxygen mole ratio of 5.6. This yield could undoubtedly be substantially increased, as discussed above.

Conclusions

The reactions which are considered of importance here are summarized in Table V. Under the conditions of this work the results indicate that a key reaction occurs between the propyl radical and oxygen, which may follow two alternate paths, one forming oxygenated organic products and the other forming propylene and the perhydroxy radical. The perhydroxy radical reacted with propane, or another hydrocarbon, to form hydrogen peroxide and a free radical. The disappearance of hydrogen peroxide during the reaction is attributed to a wall decomposition forming water and oxygen. The reactions which form the oxygenated organic products are adequately interpreted by the reaction mechanism proposed by Lewis and Von Elbe (17). The oxidation of the aldehydes also is accounted for by their mechanism, but the results of this work did not give conclusive evidence in this respect. The reactions which form the oxygenated

Table V

Reactions of Significance in the Partial Oxidation of Propane

$$C_3H_8 + O_2 \longrightarrow \text{n-and iso-} C_3H_7{}^{\cdot} + HO_2{}^{\cdot} \tag{1}$$

$$\text{n-}C_3H_7{}^{\cdot} \longrightarrow C_2H_4 + CH_3{}^{\cdot} \tag{1}$$

$$\text{n-and iso-} C_3H_7{}^{\cdot} + O_2 \longrightarrow C_3H_6 + HO_2{}^{\cdot} \tag{2}$$

$$C_3H_8 + HO_2{}^{\cdot} \longrightarrow \text{n- and iso-} C_3H_7{}^{\cdot} + H_2O_2 \tag{3}$$

$$H_2O_2 \xrightarrow{\text{wall}} H_2O + 1/2\, O_2 \tag{4}$$

$$\text{iso -} C_3H_7{}^{\cdot} + O_2 \longrightarrow [\text{iso -} C_3H_7OO] \tag{5}$$

$$[\text{iso -} C_3H_7OO] \longrightarrow CH_3CHO + CH_3O{}^{\cdot} \tag{6}$$

$$CH_3O{}^{\cdot} + C_3H_8 \longrightarrow CH_3OH + \text{n- and iso -} C_3H_7{}^{\cdot} \tag{7}$$

$$CH_3O{}^{\cdot} + O_2 \longrightarrow CO + H_2O + OH{}^{\cdot} \tag{8}$$

$$\text{n -} C_3H_7{}^{\cdot} + O_2 \longrightarrow [\text{n -} C_3H_7OO{}^{\cdot}] \tag{9}$$

$$[\text{n -} C_3H_7OO] \longrightarrow [CH_3CH_2CHO] + OH{}^{\cdot} \tag{10}$$

$$[CH_3CH_2CHO] \longrightarrow C_2H_6 + CO \tag{11}$$

$$CH_3CHO + R{}^{\cdot} \longrightarrow CH_3CO{}^{\cdot} + RH \tag{12}$$

$$CH_3CO{}^{\cdot} \longrightarrow CH_3{}^{\cdot} + CO \tag{13}$$

$$CH_3{}^{\cdot} + C_3H_8 \longrightarrow CH_4 + \text{n- and iso-} C_3H_7{}^{\cdot} \tag{14}$$

$$CH_3{}^{\cdot} + O_2 \longrightarrow HCHO + OH{}^{\cdot} \tag{15}$$

$$OH{}^{\cdot} + C_3H_8 \longrightarrow H_2O + \text{n- and iso-} C_3H_7{}^{\cdot} \tag{16}$$

$$HCHO + R{}^{\cdot} \longrightarrow HCO{}^{\cdot} + RH \tag{17}$$

$$HCO{}^{\cdot} \longrightarrow H{}^{\cdot} + CO \tag{18}$$

$$H{}^{\cdot} + C_3H_8 \longrightarrow H_2 + \text{n- and iso-} C_3H_7{}^{\cdot} \tag{19}$$

organic products are inadequate to account for the quantities
of water and hydrogen peroxide which are formed. It is
necessary to include in the reaction mechanism a reaction,
such as (2), which will connect the olefin production wit' that
of water. The negative temperature coefficient of the
reaction rate can be explained on the basis of the two
alternate reactions of the propyl radical with oxygen. With
an increase in temperature, the reaction forming propylene
increases relative to that forming oxygenated organics, and
since the products of the first reaction are less reactive, this
results in a decrease in the over-all rate in the region
375° to 475°C.

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